GEOMICROBIOLOGICAL TREATMENT FOR ENGINEERED AND NATURAL ATTENUATION OF CHLORINATED ORGANICS

Lonnie Kennedy
Earth Science Services, Inc
Oklahoma City, OK 73172-0438

Coauthor:
Jess W. Everett, Rowan University

Introduction

In oxidized subsurface environments, chlorinated ethenes such as perchloroethylene (PCE), trichloroethylene (TCE), and dichloroethylene (DCE) are recalcitrant to microbial degradation. This is because 1) such compounds are not naturally occurring so bacteria have no ready enzymatic mechanisms to degrade them and 2) chlorinated ethenes are largely oxidized molecules so they are poor substrate for heterotrophic bacteria that conserve chemical energy via redox reactions. The degradation of chlorinated ethenes appears to follow two major routes, both requiring the presence of a labile or semi labile organic. These include 1) Enzymatic Reductive Dechlorination (ERD) and 2) Biogeochemical Reductive Dechlorination (BiRD). For the ERD pathway, bacteria oxidize a labile substrate (e.g. vegetable oil) while using chlorinated ethenes as an electron acceptor compound facilitating reductive dechlorination. For BiRD, SO_4^{2-} reducing bacteria are stimulated to produce reduced FeS minerals which dechlorinate chlorinated ethenes abiotically. Both chlorinated ethene treatment routes occur naturally and both can be augmented by engineered design for in-situ bioremediation. This presentation compares ERD and BiRD, gives field examples from Altus Air Force Base, shows the results of recent laboratory experimentation, and suggests ways to quantify BiRD for natural attenuation and engineered bioremediation.

Enzymatic Reductive Dechlorination

ERD requires the addition of a labile electron donor. Common aqueous electron acceptors are generally consumed in a serial manner (O_2 > NO_3^- > SO_4^{2-} > Fe^{3+} > methanogenesis) as a function of sequentially lower free energy associated with each successive redox couple. Because PCE and TCE are oxidized compounds, certain bacterial groups are capable of utilizing them as analogs for naturally occurring electron acceptors. Thus, PCE and TCE can be reduced as a coupled reaction with the oxidation of a labile organic, i.e., reductive dechlorination. In sequence, PCE and TCE can be used as alternative electron acceptors after much of the SO_4^{2-} has been depleted but normally before Fe^{3+} reduction and methanogenesis.

There are characteristics markers that can be found in an aqueous system that indicate ERD is an active pathway for the natural attenuation chlorinated ethenes. For this route, dechlorination is stepwise, meaning PCE is dechlorinated to TCE then to DCE and finally VC. As TCE disappears there can be corresponding increases in DCE and/or VC concentrations along the plume flow path. This approach is probably limited in high SO_4^{2-} environments due to electron acceptor competition. Limitations to the ERD pathway include: 1) PCE/TCE oxidation occurs when the aquifer is significantly reduced, after O_2, NO_3^- and most SO_4^{2-} have been removed; 2) Relatively large amounts of organic may be needed to meet the oxidative capacity of the aquifer system; 3) The chlorinated ethene, electron donor, and bacteria must be in contact simultaneously, resulting in mixing requirements that may be difficult to attain in the subsurface; 4) The required high concentrations of viscous organic substrate plug permeability and block chlorinated ethenes from passing through the treatment zone; 5) Long lag times are required for bacteria to develop necessary enzymatic mechanisms/populations to reductively dechlorinate chlorinated ethenes; 6) Bacteria capable of facilitating complete dechlorination may not be present in the aquifer, making bioaugmentation necessary; 7) chlorinated ethenes do not strongly inhibit fermentation, so much of the added organic may be wasted on methanogenesis rather than its intended purpose; and 8) The daughter products, including VC, are more hazardous than the parent compound.

Biogeochemical Reductive Dechlorination (BiRD)

This approach is biogeochemical because microbial processes are used to facilitate geochemical conditions causing the precipitation of FeS minerals in the aquifer that rapidly and spontaneously reduce chlorinated ethenes through abiotic chemical processes. When labile organics are introduced to a soil/aquifer system a redox series

may develop where native soil bacteria oxidize the released organic while reducing available electron acceptors. It can be demonstrated that for many aquifers little O_2 and NO_3^- exist relative to SO_4^{2-} and Fe^{3+}. Thus, the majority of microbial oxidation processes may be expected to involve SO_4^{2-} and Fe^{3+} reduction.

The geochemistry associated with SO_4^{2-} reduction is of special interest as the respiratory product (H_2S) is chemically reactive. Oxidation of the organic via by SO_4^{2-} reducing bacteria initially produces hydrogen sulfide (H_2S) according to the reaction:

(1) $CH_2O + 0.5\ SO_4^{2-} => HCO_3^- + 0.5\ H_2S\ (g)$
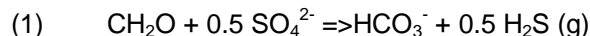
Most sediments contain large concentrations of available Fe^{3+} oxide/hydroxide minerals. Those minerals provide a strong chemical sink for H_2S forming various iron sulfide minerals as, for example, with goethite:

(2) $2FeOOH\ (s) + 3\ H_2S\ (aq) => 2FeS\ (s) + S^o + 4H_2O$
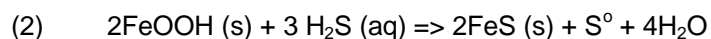
This reaction is almost instantaneous and reduces Fe^{3+} to Fe^{2+} abiotically. With time FeS is converted to FeS_2 as:

(3) $FeS\ (s) + S^o => FeS_2$
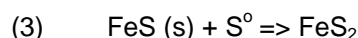
Therefore, Equations 2 and 3 show that 50% to 66% of the reduced SO_4^{2-} can precipitate as FeS with the remaining 33% to 50% as either S^o or FeS_2. Both S^o and FeS_2 are more chemically stable relative to FeS which is quite reactive. The rapid generation of FeS minerals in native sediment amended with volatile fatty acids and SO_4^{2-} is shown in Figure 1 (Kennedy and Everett 2001). Significant concentrations of FeS have been observed at several field sites which have been accidentally contaminated with organic compounds (Kennedy and Everett, 2000 and Kennedy et al., 1999). Concentrations of up to 160 mg/Kg FeS have been generated by SO_4^{2-} reducing bacteria in microcosms (Kennedy and Everett 2001).

Artificial FeS has been shown to react with TCE and PCE to facilitate complete dechlorination (Butler and Hayes, 1999). It is very noteworthy that VC is not produced by this reaction, nor does DCE accumulate. Laboratory tests with artificial FeS yield TCE degradation half-lives ranging from 19 to 27 days.

The complete oxidation of FeS by TCE would be expressed as:

(4) $4/9FeS + C_2HCl_3 + 28/9\ H_2O => 4/9\ Fe(OH)_3 + 4/9\ SO_4^{2-} + C_2H_2 + 3Cl^- + 35/9H^+$

Work by Lee and Batchelor (2002) indicates that FeS_2 also reductively dechlorinated chlorinated ethenes, making the BiRD process even more effective.

Field Observations at Altus AFB

A field study was conducted at Altus Air Force Base to examine the engineered and natural attenuation potential for BiRD. Soil and groundwater was impacted by fuels from an underground storage tank facility near the source area of a TCE release. The native sediment was high Fe^{3+} and gypsum, a $CaSO_4^{2-}$ sediment, so the groundwater is naturally saturated with SO_4^{2-}. Based on bore hole geophysical density logging, contaminants followed pervasive pathways of high porosity in the shale bedrock and at the overlying clay/shale boundary. SO_4^{2-} was diminished in the fuel release area and concentrations of FeS and FeS_2 were elevated. TCE was destroyed in the FeS mineral area with no daughter products suggesting BiRD as the dechlorination route (Figure 2).

Laboratory Experimentation at Altus AFB

A pilot scale test plot was installed at Altus AFB by Terra Systems to examine ERD using edible vegetable oil as the electron donor. One year after the plot was installed Earth Science Services and Rowan University sampled soils and conducted microcosm batch studies on sediments containing elevated FeS concentrations. Sediment was collected under anaerobic conditions. All microcosms were amended with approximately 10,000 ug/L TCE and half were sterilized by irradiation. Controls were made of TCE mixed with clean sediment. TCE was removed from both the live and killed microcosms at the same rate (~41 day half life) with corresponding destruction of FeS minerals (Figure 3). No daughter products were observed. This indicates that abiotic processes dominate TCE dechlorination at Altus AFB.

Discussion

Much observed reductive dechlorination may be due to abiotic processes which have been overlooked. Biogeochemical reductive dechlorination is the favored pathway at Altus AFB as established by both field and laboratory observations.   Recognizing the importance of the abiotic processes will improve both our understanding of natural attenuation and in-situ bioremediation potential for chlorinated ethenes.   There are several advantages to the BiRD pathway as an in-situ treatment technique including: 1) Precipitated FeS minerals act as a permeable reactive wall even after the organic and SO_4^{2-} are depleted so subsurface mixing problems are eliminated; 2) High SO_4^{2-} inhibits methanogenesis by electron acceptor competition reducing required organic concentrations; 3) The organic need not be viscous and does not plug aquifer pore space or reduce permeability; 4) SO_4^{2-} bacteria are ubiquitous in the subsurface so there is no need for bioaugmentation; 5) Microbial enzymatic mechanisms for SO_4^{2-} reduction exist so there is little lag time in FeS mineral generation; 6) FeS formation is instantaneous reacting HS- with native Fe^{3+} minerals usually in abundance; 8) Dechlorination is rapid (19 to 41 day half life); 9) No chlorinated daughter products are formed.

Although BiRD may require the addition of both organic and SO_4^{2-} both will be removed from the aquifer system. The organic will normally be oxidized to CO_2 while respired SO_4^{2-} will drop out of solution as a mineral FeS. Though mineral FeS will ultimately oxidize back to Fe^{3+} and SO_4^{2-} the rate of reentry to the aquifer is dependent on the flux of oxidized compounds (O_2, NO_3^-, and chlorinated ethenes).   Thus, SO_4^{2-} will normally be slowly released back to the aquifer. Organic and SO_4^{2-} can be introduced to the aquifer via temporary injection wells or other mechanisms.

References
Butler, E. C., and K. F. Hayes, 1999. Kinetics of the transformation of trichloroethylene and tetrachloroethylene by iron sulfide, Environmental Science and Technology, 33:2021-2027.

Kennedy L.G., J.W. Everett, 2001. Microbial degradation of simulated landfill leachate: Solid iron/sulfur interactions, Applied Environmental Research, Vol 5/2,   pp 103-116.

Kennedy L.G., J.W. Everett, K. J. Ware, and V. Green, 1999. Methods for analyzing iron and iron sulfide, minerals for natural attenuation assessment with field examples, Bioremediation Journal, 3:259-275.

Lee, W. and B. Batchelor, 2002. Abiotic reductive dechlorination of chlorinated ethenes by iron-bearing soil minerals. 1. Pyrite and magnetite, Environmental Science and Technology. 36: 5247-5154.
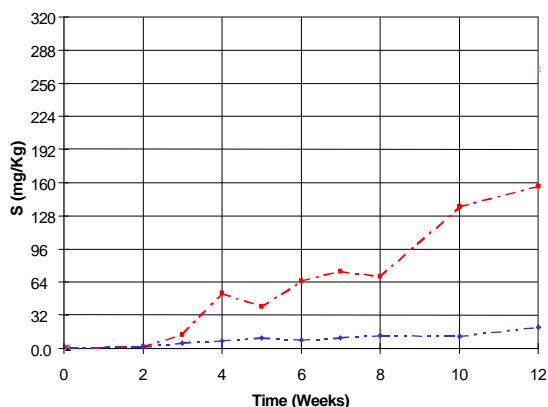
Figure 1: Microbial production of iron sulfide in microcosm
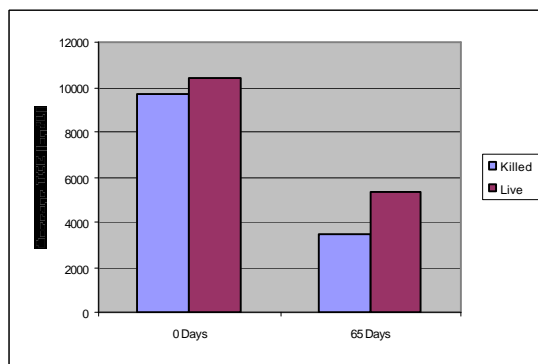
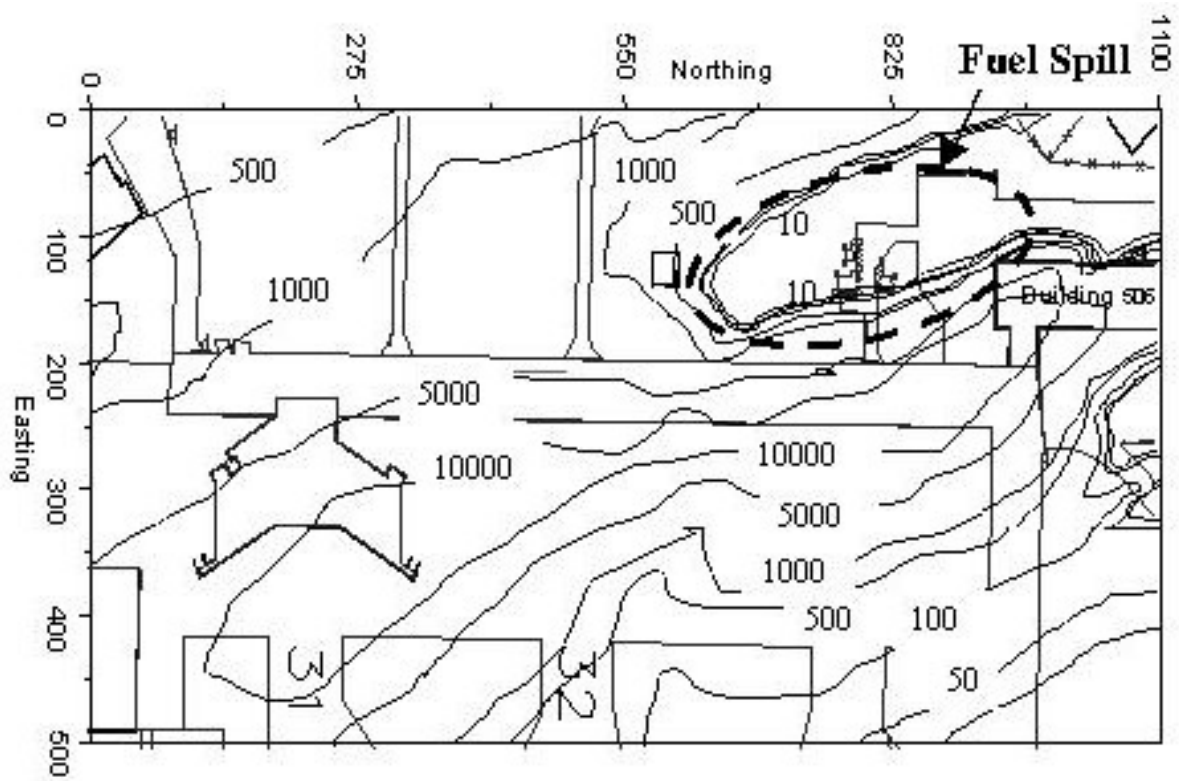

Figure 3: TCE degradation by microbe-generated FeS

Figure 2: TCE Plume at Altus AFB (ug/l) adjacent to Fuel Spill